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(54) USE OF AXIAL SUBSTITUTED PHTHALOCYANINE COMPOUND FOR PREPARING ORGANIC THIN-FILM TRANSISTOR

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(51) **Int. Cl.**

 $H01L\ 51/40$ (2006.01)

See application file for complete search history.

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(57) ABSTRACT

This invention relates to the use of axial substituted phthalocyanine compound as a semiconductor layer between the source/drain electrodes of organic thin-film transistor. The centre ligand of the axial substituted phthalocyanine compound is an atom with 3 valences or higher, and the axial ligands are chlorine, fluorine, or oxygen which can be connected with the centre ligands of axial substituted phthalocyanine compounds. Crystalline Film with high quality can be prepared on an organic substrate from the axial substituted phthalocyanine compound using vapor deposition process. These crystalline films have high carrier mobility, rich energy level, and stable performances and are easy for integrated process. The field effect mobility and the on/off Ratio of the organic thin-film transistor are 0.01 cm²/Vs or more and higher than 10⁵, respectively.

4 Claims, 3 Drawing Sheets

(a)

24 25 N N N 8 8 9 18 15 L 15 L

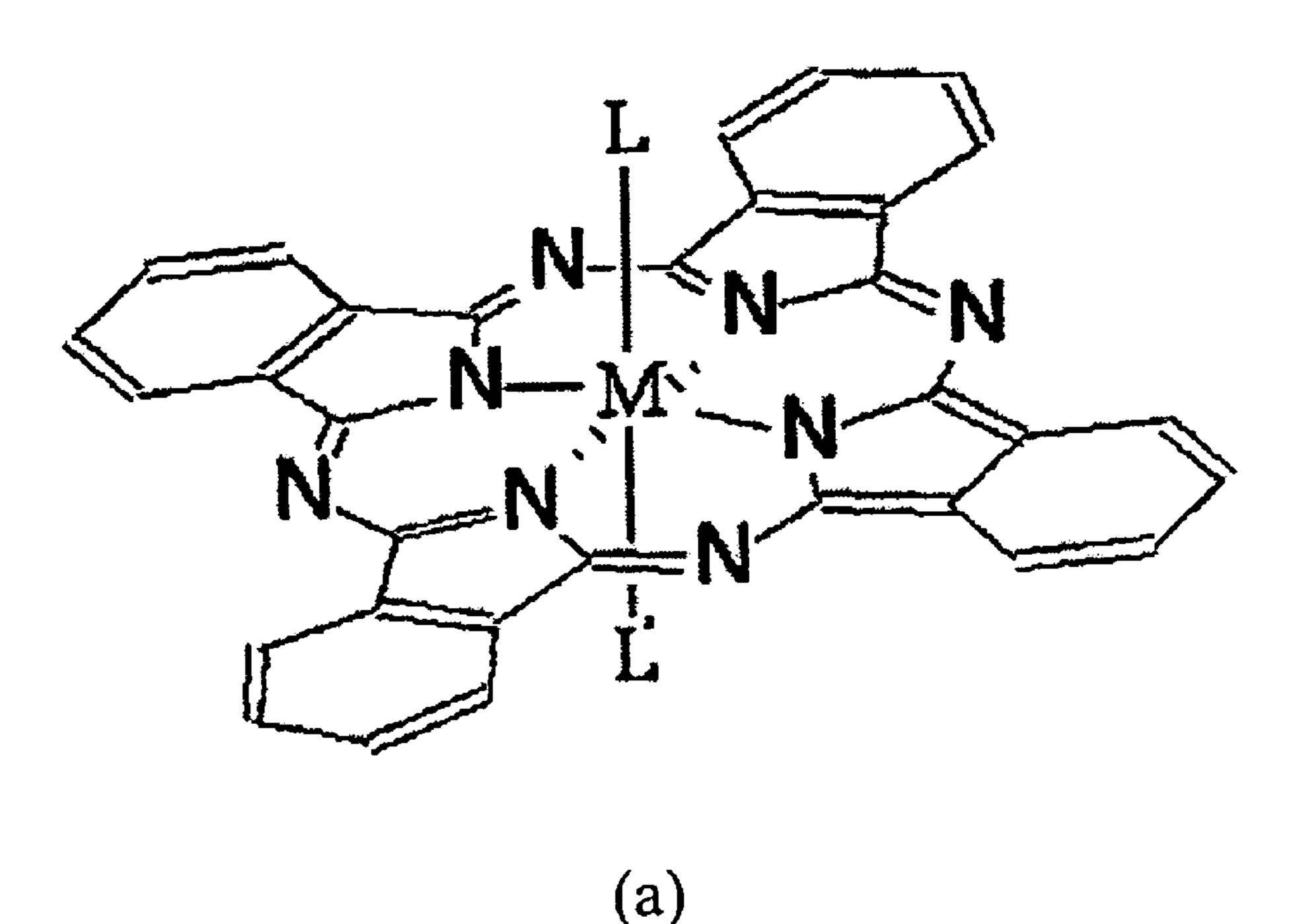
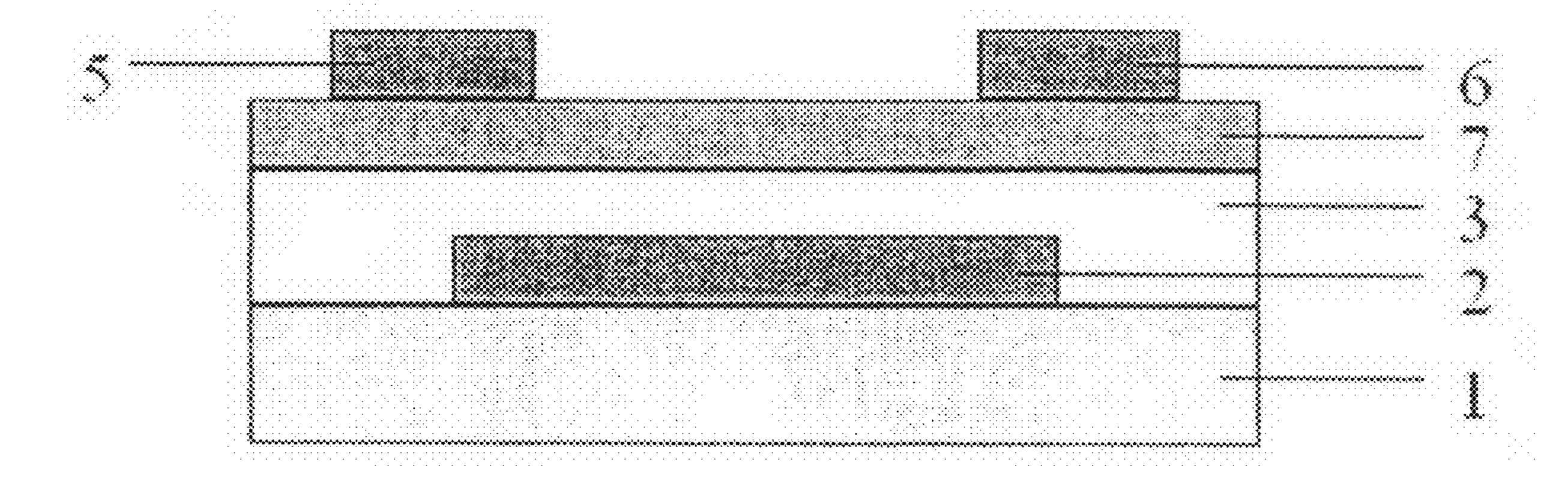


FIG. 1



PIG. 2

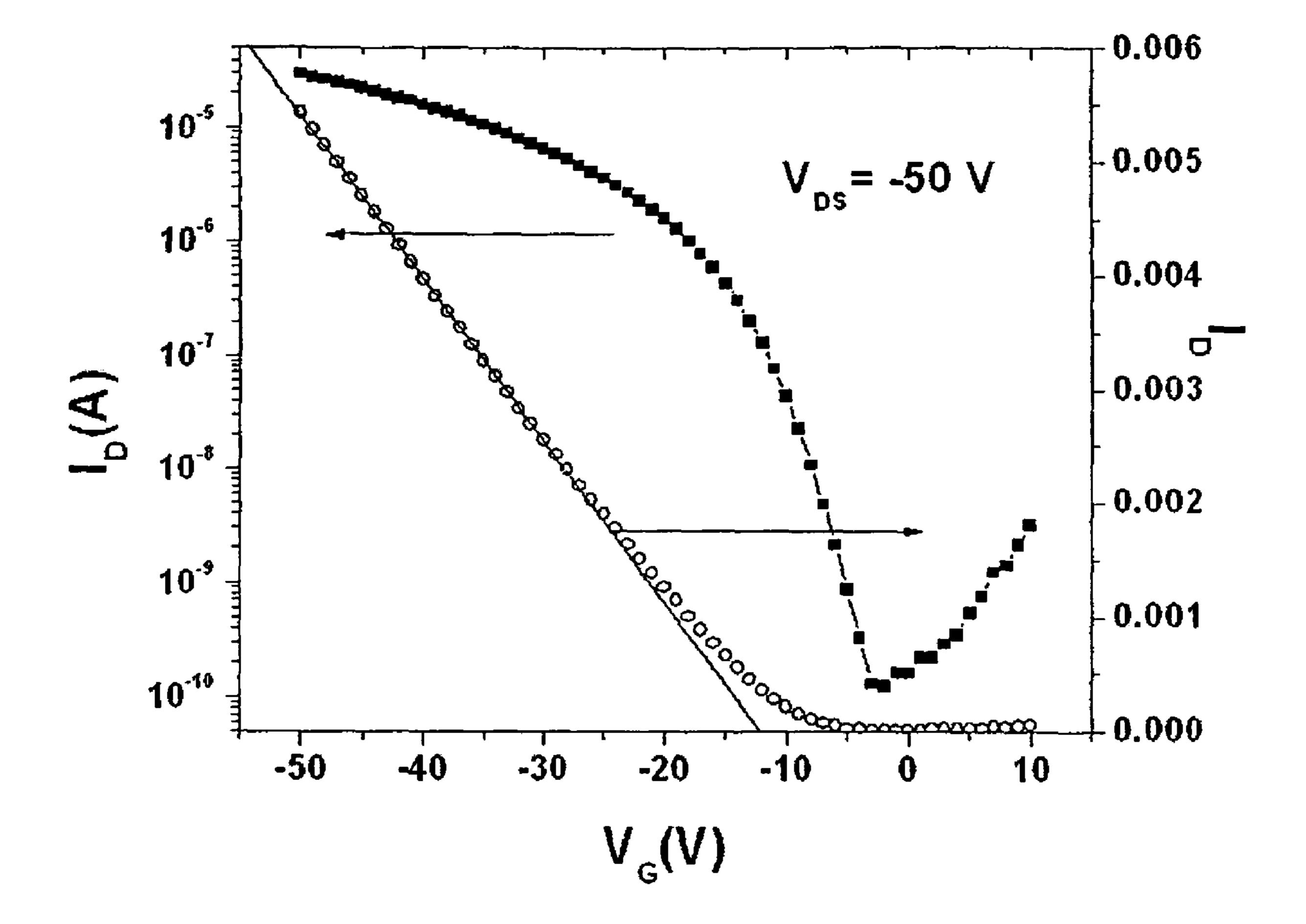


FIG. 3

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USE OF AXIAL SUBSTITUTED PHTHALOCYANINE COMPOUND FOR PREPARING ORGANIC THIN-FILM TRANSISTOR

FIELD OF THE INVENTION

The present invention relates to the use of axial substituted phthalocyanine compound for preparing organic thin-film transistor.

DESCRIPTION OF THE RELATED ART

Organic semiconductors with the property of high carrier mobility have application prospects in the applications of information display, integrated circuits, photovoltaic cells and sensors etc. However, at present most of the organic semiconductors show sensitivity to circumstances, which brings great difficulties to the integrated processing and application of organic electronic devices. U.S. Pat. No. 5,969,376 disclosed a p-channel organic thin-film transistor using planar metal phthalocyanines [copper phthalocyanine (CuPc), zinc phthalocyanine (ZnPc), free phthalocyanine (H2Pc), stannum phthalocyanine (SnPc)]. In 1998, Journal of the American Chemical Society (J. Am. Chem. Soc. 1998, 120, 207-208) reported an n-channel organic thin-film transistor using planar metal phthalocyanines [metal hexadecafluoro phthalocyanine (F16MPc), ferrum hexadecachloro phthalocyanine (Cl16FePc), octacyano substituted copper phthalocyanine ((CN)8CuPc)]. In 2006, Applied Physics Letter (Appl. Phys. Lett. 89, 163516 (2006)) reported an n-channel organic thin-film transistor using planar metal phthalocyanines [copper hexadecachloro phthalocyanine (Cl16CuPc)]; Chinese Patent No. 02129458.5 disclosed a p-channel organic thin-film transistor using nonplanar metal phthalocyanines [titanium oxygen phthalocyanine (TiOPc), vanadium oxygen phthalocyanine (VOPc)]. These organic semiconductors with mobility of 10-3 cm²/Vs or more are not sensitive to circumstances, work steadily and are suitable for integrated process. In order to further meet the demand of the development of organic electronic devices, it is required to further enhance and enrich the carrier mobility and the electron structures of semiconductors.

SUMMARY OF THE INVENTION

The invention aims to provide the use of axial substituted phthalocyanine compound for preparing organic thin-film transistor, and relates to the use of axial substituted phthalocyanine compound for preparing the semiconductor layer between the source and drain electrodes of organic thin-film 50 transistor. The field effect mobility and the on/off ratio of the organic thin-film transistor using axial substituted phthalocyanine compound as semiconductor layer between the source and drain electrodes are 0.01 cm² Vs or more and higher than 10⁵, respectively.

The molecular structure schemes of axial substituted phthalocyanine compounds are shown in the FIG. 1(a) and FIG. **1**(*b*).

In which: FIG. $\mathbf{1}(a)$ shows the axial substituted phthalocyanine, M represents the centre substituted ligand, and L, L' 60 represent the axial ligands, wherein L and L' can be the same or different from each other; and FIG. 1(b) shows the positions of the substituents on phenyl group: the substituted atoms of 1, 2, 3, 4, 8, 9, 10, 11, 15, 16, 17, 18, 22, 23, 24, 25 can be fluorine (F), chlorine (Cl). As an example, chloroalu- 65 minum hexadecachloro phthalocyanine (Cl₁₆AlClPc) can be mentioned.

The centre ligand of axial substituted phthalocyanine compounds is an atom with 3 valences or more, and the axial ligands are chlorine (Cl), fluorine (F), oxygen (O) which can be connected with the centre ligands of axial substituted 5 phthalocyanine compounds.

The principle of the invention is that centre ligand and axial ligand can adjust the electron structure of axial substituted phthalocyanine.

The axial substituted phthalocyanine compound is one selected from the group consisting of indium fluorine phthalocyanine (InFPc), titanium difluorine phthalocyanine (TiF₂Pc), stannum difluorine phthalocyanine (SnF₂Pc), ferrum chlorine phthalocyanine (FeClPc), indium chlorine phthalocyanine (InClPc), gallium chlorine phthalocyanine 15 (GaClPc), manganese chlorine phthalocyanine (MnClPc), stannum oxygen phthalocyanine (SnOPc), titanium dichlorine phthalocyanine (TiCl₂Pc), stannum dichlorine phthalocyanine (SnCl₂Pc), germanium dichlorine phthalocyanine (GeCl₂Pc), oxygen titanium hexadecafluoro phthalocyanine (F₁₆TiOPc), oxygen titanium hexadecachloro phthalocyanine (Cl₁₆TiOPc), oxygen vanadium hexadecafluoro phthalocyanine (F₁₆VOPc), oxygen vanadium hexadecachloro phthalocyanine (Cl₁₆VOPc), indium chlorine hexadecafluoro phthalocyanine (F₁₆InClPc), indium chlorine hexadecachloro phthalocyanine (Cl₁₆InClPc), stannum dichlorine hexadecafluoro phthalocyanine (F₁₆SnCl₂Pc), stannum dichlorine hexadecachloro phthalocyanine (Cl₁₆SnCl₂Pc), hexadecafluoro phthalocyanine dichlorine titanium (F₁₆TiCl₂Pc), manganese chlorine hexadecafluoro phthalo-30 cyanine (F₁₆MnClPc), aluminium chlorine hexadecafluoro phthalocyanine (F₁₆AlClPc) and aluminium chlorine hexadecachloro phthalocyanine (Cl₁₆AlClPc).

The thickness of the semiconductor layer between the source and drain electrodes of the organic thin-film transistor 35 prepared from said axial substituted phthalocyanine compound is between 10-50 nm.

Crystalline film with high quality can be prepared on organic substrate from said axial substituted phthalocyanine compound using vapour deposition process. These crystalline films have high carrier mobility, rich energy level, stable performances and are easy for integrated process. The field effect mobility and the on/off ratio of the organic thin-film transistor using axial substituted phthalocyanine compound as the semiconductor layer between the source and drain electrodes are no less than $0.01 \text{ cm}^2/\text{Vs}$ and higher than 10^5 , respectively.

The structure of the organic thin-film transistor using axial substituted phthalocyanine compound as the semiconductor layer between the source and drain electrodes is shown in FIG. 2 in which: (1) represents substrate, (2) grid, (3) insulated gate layer, (5) and (6) source electrode and drain electrode, (7) semiconductor layer of the axial substituted phthalocyanine compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the molecular structure formula of the axial substituted phthalocyanine compound, in which: FIG. 1(a)shows the axial substituted phthalocyanine, M represents the centre substituted ligand, and L, L' represent the axial ligands, wherein L and L' can be the same or different from each other (for example, titanium dichlorine phthalocyanine (TiCl₂Pc)); and (b) shows the positions of the substituents on phenyl group: the substituted atoms of 1, 2, 3, 4, 8, 9, 10, 11, 15, 16, 17, 18, 22, 23, 24, 25 can be fluorine (F), chlorine (Cl) (for example aluminum chlorine hexadecachloro phthalocyanine $(Cl_{16}AlClPc)$.

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FIG. 2 shows the structural scheme of the thin-film transistor, wherein, (1) represents substrate, (2) grid, (3) insulated gate layer, (5) and (6) source and drain electrodes, (7) semiconductor layer of the axial substituted phthalocyanine compound.

FIG. 3 shows the transfer characteristic curve of TiCl₂Pc.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention will be described below in combination with appended drawings. FIG. 2 is one example of the structure using top-touch type thin-film transistor of the organic semiconductor according to the present invention.

Example 1

The tantalum pentoxide (Ta₂O₅), silicon dioxide (SiO₂) and aluminum oxide (Al₂O₃) targets, and the gold (Au) and aluminum (Al) metal electrodes used in the example are commercial products, and can be used directly. Glass substrates and plastic substrates are commercial products and can be used after cleaning. The ferrum chlorine phthalocyanine (FeClPc), titanium dichlorine phthalocyanine (TiCl₂Pc), stannum dichlorine phthalocyanine (SnCl₂Pc), indium chlorine phthalocyanine (InClPc), manganese chlorine phthalocyanine (Ga-ClPc), stannum oxygen phthalocyanine (SnOPc) used as the axial substituted phthalocyanine compounds in the example are commercial products and can be used after purification.

Polymethyl methacrylate (PMMA) is commercial product, and was formulated into 3-0.5 wt % butanone solution for use.

A layer of metal chromium (Cr) film with the thickness of about 200 nm was plated on 7059 glass substrate or flexible plastic substrate (1) by radio frequency magnetron sputtering method, and was photoetched into grid (2); on grid (2), a layer of tantalum pentoxide (Ta₂O₅), silicon dioxide (SiO₂) or aluminum oxide (Al₂O₃) was formed as insulated gate layer (3) with the thickness of about 100 nm by magnetron sputtering method, and PMMA with the thickness of 50 nm was spinning coated on the surface of insulated gate layer (3); then semiconductor (7) with the thickness of 10 to 30 nm was grown by molecule vapour deposition process at the temperature between 25 to 250° C., source and drain electrodes (5) and (6) of gold (Au) and aluminum (Al) with the thickness of 20-50 nm were then deposited.

The source and drain electrodes, surface modification layer, and properties of the carrier mobility (cm²/Vs), types of the carriers, and on/off current ratio of thin-film transistor are listed in Table 1.

TABLE 1

Source and drain electrodes of thin-film transistor device, and

properties of carrier mobility (cm²/Vs), types of the carriers

and on/off current ratio of the thin-film transistor device					
source and drain electrodes	carrier mobility	carrier type	on/off current ratio		
Au	0.15	hole	10 ⁵		
Al	0.16	electron	10^{5}	_	
Au	0.14	electron	10^{5}	6	
Au	0.011	hole	10 ⁵		
Au	0.025	hole	10^{5}		
Au	0.011	hole	10^{5}		
Au	0.010	hole	10 ⁵		
Al	0.017	electron	10^{5}		
Au	0.020	electron	10^{5}	6	
	source and drain electrodes Au Al Au	source and drain electrodes carrier mobility Au 0.15 Al 0.16 Au 0.14 Au 0.011 Au 0.025 Au 0.010 Al 0.017	source and drain electrodes mobility type Au 0.15 hole Al 0.16 electron Au 0.14 electron Au 0.011 hole Au 0.025 hole Au 0.011 hole Au 0.011 hole Au 0.010 hole Al 0.017 electron	source and drain electrodescarrier mobilitycarrier typeon/off current ratioAu 0.15 hole 10^5 Al 0.16 electron 10^5 Au 0.14 electron 10^5 Au 0.011 hole 10^5 Au 0.025 hole 10^5 Au 0.011 hole 10^5 Au 0.010 hole 10^5 Au 0.010 hole 10^5 Al 0.017 electron 10^5	

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Example 2

Tantalum pentoxide (Ta_2O_5), silicon dioxide (SiO_2) and aluminum oxide (Al₂O₃) used as targets in the example and gold (Au) and aluminum (Al) metal electrodes in the example are commercial products and can be used directly. Glass substrates and plastic substrates are commercial products and can be used after cleaning. Titanium difluorine phthalocyanine (TiF₂Pc), stannum difluorine phthalocyanine (SnF₂Pc), indium fluorine phthalocyanine (InFPc), germanium dichlorine phthalocyanine (GeCl₂Pc), oxygen titanium hexadecafluoro phthalocyanine (F₁₆TiOPc), oxygen vanadium hexadecafluoro phthalocyanine (F₁₆VOPc), indium chlorine hexadecafluoro phthalocyanine (F₁₆InClPc), manganese chlorine hexadecafluoro phthalocyanine (F₁₆MnClPc), standichlorine hexadecafluoro phthalocyanine num (F₁₆SnCl₂Pc), titanium dichlorine hexadecafluoro phthalocyanine (F₁₆TiCl₂Pc), aluminium chlorine hexadecafluoro phthalocyanine (F₁₆AlClPc), aluminium chlorine hexadecachloro phthalocyanine (Cl₁₆AlClPc), stannum dichlorine hexadecachloro phthalocyanine (Cl₁₆SnCl₂Pc), oxygen titanium hexadecachloro phthalocyanine (Cl₁₆TiOPc), oxygen vanadium hexadecafluoro phthalocyanine (Cl₁₆VOP_c), hexadecachloro indium chlorine phthalocyanine (Cl₁₆InClPc) were synthesized according to literature (*Inorg.*) Chem. 1962, 1, 331-333; Inorganica Chimica Acta 1999, 293, 80-87).

A layer of metal chromium (Cr) film with the thickness of about 200 nm was plated on 7059 glass substrate or flexible plastic substrate (1) by radio frequency magnetron sputtering method, and was photoetched into grid (2); on grid (2) a layer of tantalum pentoxide (Ta₂O₅), silicon dioxide (SiO₂) or aluminum oxide (Al₂O₃) as insulated gate layer (3) with the thickness of about 100 nm was formed by magnetron sputtering method, and the surface of insulated gate layer (3) was modified by octadecyltrichlorosilane (hereinafter referred to as OTS), or was deposited with para-sexiphenyl (hereinafter referred to as 6P) by vacuum deposition; then semiconductor (7) with the thickness of 10 to 30 nm was grown by molecule vapor deposition process at the temperature between 25 to 250° C., and then the source and drain electrodes (5) and (6) of gold (Au) and aluminum (Al) with the thickness of 20-50 nm was also deposited.

The source and drain electrodes, surface modification layer, properties of the carrier mobility, and on/off current ratio of the thin-film transistor device are listed in Table 2.

TABLE 2

Source and drain electrodes, surface modification layer, properties of carrier mobility (cm²/Vs), carrier types and on/off current ratio of the thin-film transistor device

50						
	Organic semiconductor	source and drain electrodes	surface modification layer	carrier mobility	carrier type	on/off current ratio
	F ₁₆ AlClPc	Al	OTS	0.012	electron	10 ⁵
55	F ₁₆ AlClPc	Al	6P	0.023	electron	10^{5}
	F ₁₆ AlClPc	Au	OTS	0.010	electron	10^{5}
	F ₁₆ AlClPc	Al	6P	0.017	electron	10^{5}
	F ₁₆ MnClPc	Al	OTS	0.016	electron	10^{5}
60	F ₁₆ MnClPc	Al	6P	0.014	electron	10^{5}
	F ₁₆ MnClPc	Au	OTS	0.012	electron	10^{5}
	F ₁₆ MnClPc	Au	6P	0.021	electron	10^{5}
	F ₁₆ InClPc	Al	OTS	0.015	electron	10^{5}
	F ₁₆ InClPc	Al	6P	0.21	electron	10^{5}
	F ₁₆ InClPc	Au	OTS	0.012	electron	10^{5}
	F ₁₆ InClPc	Au	6P	0.27	electron	10^{5}
65	F ₁₆ SnCl ₂ Pc	Al	OTS	0.010	electron	10^{5}
	F ₁₆ SnCl ₂ Pc	Al	6P	0.11	electron	10^{5}
	F ₁₆ SnCl ₂ Pc	Au	OTS	0.013	electron	10^{5}
	F ₁₆ SnCl ₂ Pc	Au	6P	0.24	electron	10^{5}

Source and drain electrodes, surface modification layer, properties of carrier mobility (cm²/Vs), carrier types and on/off current ratio of the thin-film transistor device

Organic semiconductor	source and drain electrodes	surface modification layer	carrier mobility	carrier type	on/off current ratio
F ₁₆ TiCl ₂ Pc	Al	OTS	0.011	electron	10 ⁵
F ₁₆ TiCl ₂ Pc	Al	6P	0.021	electron	10^{5}
F ₁₆ TiCl ₂ Pc	Au	OTS	0.017	electron	10^{5}
F ₁₆ TiCl ₂ Pc	Au	6P	0.26	electron	10^{5}
F ₁₆ TiOPc	Al	OTS	0.11	electron	10^{5}
F ₁₆ TiOPc	Al	6P	0.20	electron	10^{5}
F ₁₆ TiOPc	Au	OTS	0.21	electron	10^{5}
F ₁₆ TiOPc	Au	6P	0.43	electron	10^{5}
F ₁₆ VOPc	Al	OTS	0.12	electron	10^{5}
F ₁₆ VOPc	Al	6P	0.17	electron	10^{5}
F ₁₆ VOPc	Au	OTS	0.23	electron	10^{5}
F ₁₆ VOPc	Au	6P	0.39	electron	10^{5}
Cl ₁₆ SnCl ₂ Pc	Al	OTS	0.012	electron	10^{5}
Cl ₁₆ SnCl ₂ Pc	Al	6P	0.017	electron	10^{5}
Cl ₁₆ SnCl ₂ Pc	Au	OTS	0.023	electron	10^{5}
Cl ₁₆ SnCl ₂ Pc	Au	6P	0.17	electron	10^{5}
Cl ₁₆ AlClPc	Al	OTS	0.014	electron	10^{5}
Cl ₁₆ AlClPc	Al	6P	0.022	electron	10^{5}
Cl ₁₆ AlClPc	Au	OTS	0.013	electron	10^{5}
Cl ₁₆ AlClPc	Au	6P	0.017	electron	10^{5}
Cl ₁₆ InClPc	Al	OTS	0.015	electron	10^{5}
Cl ₁₆ InClPc	Al	6P	0.019	electron	10^{5}
Cl ₁₆ InClPc	Au	OTS	0.16	electron	10^{5}
Cl ₁₆ InClPc	Au	6P	0.21	electron	10^{5}
Cl ₁₆ VOPc	Al	OTS	0.010	electron	10^{5}
Cl ₁₆ VOPc	Al	6P	0.073	electron	10^{5}
Cl ₁₆ VOPc	Au	OTS	0.042	electron	10^{5}
Cl ₁₆ VOPc	Au	6P	0.37	electron	10^{5}
Cl ₁₆ TiOPc	Al	OTS	0.012	electron	10^{5}
Cl ₁₆ TiOPc	Al	6P	0.012	electron	10^{5}
Cl ₁₆ TiOPc	Au	OTS	0.016	electron	10^{5}
Cl ₁₆ TiOPc	Au	6P	0.023	electron	10^{5}
SnF_2Pc	Al	OTS	0.010	electron	10^{5}
SnF_2Pc	Al	6P	0.018	electron	10^{5}
SnF_2Pc	Au	OTS	0.051	electron	10^{5}
SnF ₂ Pc	Au	6P	0.074	electron	10^{5}
TiF ₂ Pc	Al	OTS	0.012	electron	10^{5}
TiF ₂ Pc	Al	6P	0.025	electron	10^{5}
TiF ₂ Pc	Au	OTS	0.042	electron	10^{5}
TiF ₂ Pc	Au	6P	0.085	electron	10^{5}
InFPc	Al	OTS	0.017	electron	10^{5}
InFPc	Al	6P	0.024	electron	10^{5}
InFPc	Au	OTS	0.031	electron	10^{5}
InFPc	Au	6P	0.077	electron	10^{5}
GeCl ₂ Pc	Au	OTS	0.061	hole	10^{5}
GeCl ₂ Pc	Au	6P	0.090	hole	10 ⁵

The present invention is not limited to the examples described above. Generally, the organic transistor disclosed

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in the present invention can be made into components in two dimensional or three dimensional integrated devices. These integrated devices can be used in the applications of flexible integrated circuits, active matrix display etc. The components using organic thin-film transistor according to the present invention can be processed at low temperature.

What is claimed is:

- 1. A method for preparing an organic thin-film transistor, comprising preparing a semiconductor layer between source and drain electrodes of the organic thin-film transistor using an axial substituted phthalocyanine compound, wherein the center ligand of said axial substituted phthalocyanine compound is an atom with 3 valences or higher, and the axial ligands are chlorine, fluorine, or oxygen, which can be con-15 nected with the center ligand of axial substituted phthalocyanine compounds; wherein said axial substituted phthalocyanine compound is selected from the group consisting of indium fluorine phthalocyanine, ferrum chlorine phthalocyanine, indium chlorine phthalocyanine, gallium chlorine phthalocyanine, manganese chlorine phthalocyanine, indium chlorine hexadecafluoro phthalocyanine, indium chlorine hexadecachloro phthalocyanine, manganese chlorine hexadecafluoro phthalocyanine, aluminium chlorine hexadecafluoro phthalocyanine and aluminium chlorine hexade-²⁵ cachloro phthalocyanine.
 - 2. The method according to claim 1, wherein the thickness of said semiconductor layer between the source and drain electrodes of the organic thin-film transistor is between 10-50 nm.
 - 3. A method for preparing transistor comprising preparing a semiconductor layer between source and drain electrodes of the organic thin-film transistor using an axial-substituted phthalocyanine compound, wherein the center ligand of said axial substituted phthalocyanine compound is an atom with 3 valences or higher, and the axial ligands are chlorine, fluorine, or oxygen, which can be connected with the center ligand of axial substituted phthalocyanine compounds; wherein said axial substituted phthalocyanine compound is selected from the group consisting of stannum oxygen phthalocyanine, oxygen titanium hexadecafluoro phthalocyanine, oxygen vanadium hexadecafluoro phthalocyanine, oxygen vanadium hexadecafluoro phthalocyanine, and oxygen vanadium hexadecafluoro phthalocyanine.
 - 4. The method according to claim 3, wherein the thickness of said semiconductor layer between the source and drain electrodes of the organic thin-film transistor is between 10-50 nm.

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